Solvolysis in Dipolar Aprotic Media. II.[1] Initial Rates of Bromide Ion Production from Tertiary Alkyl Bromides in Dimethylformamide, Measured *in Situ*. A Proposal of a Solvolysis Scheme for 2-Bromo-2-methylpentane[2]

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A novel compensation method, based on potentiometric detection of Br^-, has been used to measure initial solvolysis rates of RMe_2CBr in DMF (R = Me, Et, Pr) with fair precision. Influences of substrate structure and of ionic strength are comparable to the same in protic solvents. Rate enhancement by added azide and lower activation energies was noted however. Complete absence of ionic additives gave rise to an unforeseen 17% enhancement of the expected rate. These data have been combined with those obtained in the foregoing paper to allow elaboration of a scheme for the solvolysis of $PrCMe_2Br$ (1) in DMF. The possible pathways are discussed in the light of the available evidence. It is concluded that free carbenium ions are mechanistically unimportant, whereas different kinds of ion pairs are probably essential intermediates. Some un-ionized water-extractable species, formed abundantly at dissolution of the substrate, do not lie on the main reaction path. Before an autocatalytic E2 mechanism with Br^- (and HBr_2^-) becomes predominant, the major process is constituted by substitution by the solvent, probably at the solvent-separated ion-pair stage, and subsequent elimination of the cationic substitution product (7).

There exist many marked differences between protic and dipolar aprotic solvents (DAS), liable to be relevant for their role in solvolytic reactions.[3] In the foregoing paper,[1] results have been described pertaining to the DMF solvolysis of 2-bromo-2-methylpentane (1). Conventional methods or adaptations thereof were used to disclose the existence of several reaction phases, including the dominance of substitution by the solvent as a primary process and the immediate initial presence of relatively large amounts of ion pairs, suggestive of their possible importance as reaction intermediates. Since direct assessment of total solvolysis had proved impossible, no distinction could be made between extractable ion pairs and the (ionic) substitution product.

The present paper describes the elaboration of a method able to measure the formation of ionized bromide as distinguishable from any ion pairs, as it is based on potentiometric detection of its concentration in the solvent itself. It has been used to measure initial solvolysis rates of a few "simple" tertiary alkyl bromides. An attempt is made to derive a solvolysis scheme for 1 in DMF, from a combination of these results with data previously obtained[1] and from calculations based upon them.

Experimental Section

Principle of the Potentiometric Method. The apparatus is composed of two identical thermostated vessels which were filled with an equal amount of the same medium, provided with an identical electrode system and connected through an electrolyte bridge. One of these serves as a reaction vessel. As the reaction proceeds, ions are liberated, to which the electrode system responds, and the potential difference is detected. Addition of concentrated titrant to the other vessel allows restoration of the original balance, allowing the evaluation of the progress of the reaction in the proper undisturbed medium.

The Electrode System. As the method was conceived to follow bromide ion production, the electrode system chosen consists of a silver electrode in contact with a solution containing 0.001 *M* $AgBr_2^-$.[4] The stability constant of this complex has been measured by a potentiometric titration method, as described previously,[5] and found to be 0.3×10^{16} and 1×10^{16} $mol^{-2}\ l.^2$ at 30 and 60°, respectively. It is readily calculated that the initial C_{Ag^+} at 30° amounts to 4×10^{-7} *M*. Thus catalysis by silver ion is insignificant, the more so as this concentration is still substantially lowered soon after the reaction sets in.[6]

Evaluation of the Method. Apart from the fact that the method fulfills a need by determining the bromide ion produced in the solvent, it possesses several advantages. It exhibits a true specificity, a characteristic of a potentiometric method, thus enabling measurements to be carried out in the presence of other ions, even halide ions. As it is a compensation method, an exact knowledge of the value of the stability constant of the $AgBr_2^-$ is not needed, provided it remains of the same order. Even if strong complexation with Ag^+ would occur, this can at most make the method insensitive, but once measurements can be performed, no error is introduced. The sole assumption which has to be made is that of the physical equality of both solutions. As a matter of fact, this cannot be exactly so, as only one of them receives the substrate. At small concentrations however, the organic compounds are not suspected to have a marked influence on the ion activities. A further objection may be found in the nonequivalency of the counterions, but as in our case the method was only used for bromide concentrations up to 3×10^{-3} *M*, this may be safely ignored.

Application of the method may probably be extended to the determination of other halide ions (even other anions) in DMF and in other solvents such as DMSO, HMPT, acetonitrile, and even alcohols, as suggested by literature values of stability constants of the corresponding complexes[7] and the general usability of silver electrodes in most[8] solvents. The most serious limitation of the method in its present form, resides in a certain slowness of response of the electrodes (1 min for a 10-mV jump), interfering with the measurement of fast reactions. It cannot be removed by lowering the substrate concentration indefinitely, as 10^{-5} *M* is the lower limit of concentrations that can be detected with the desired swiftness.

Description of the Apparatus. The water-jacketed reaction and titration vessels, of identical construction and volume (50 ml), possess a conical side wall and flat bottom to permit magnetic stirring. They are provided with five necks of appropriate size to allow insertion of electrodes, electrolyte bridge, nitrogen inlet, and if needed a capillary buret tip. The substrate is added by injection through a septum of silicone rubber.

The salt bridge is filled with a saturated solution of $NaNO_3$ in DMF. Liquid junction is established through the spacing between the ground conical inner surface of the bridge's stem and the ground tip of a glass rod, closing it from the inside.

Electrodes consist of a silver strip (0.5 cm^2; 0.5 mm thick) welded to a platinum wire. They are activated by dipping in 7 *N* NHO_3 with some $NaNO_3$ added. At first contact with the medium, containing 10^{-3} *M* $AgBr_2^-$, an adaption period of 10–15 min is re-

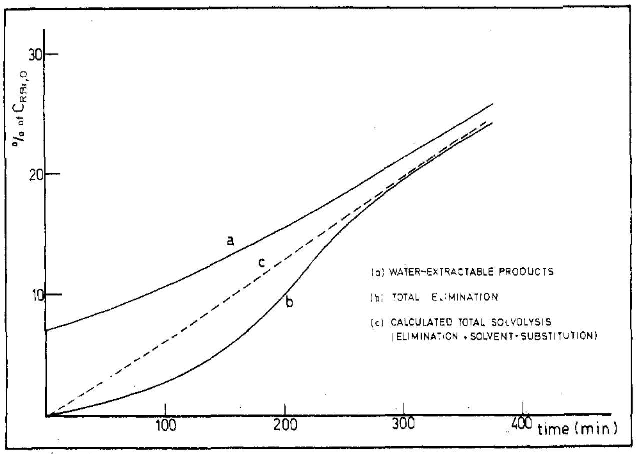


Figure 1. Comparison of experimental data (ref 1, Figure 3) on the solvolysis of 1 in DMF at 30.0° with the calculated total solvolysis (*i.e.*, total elimination plus solvent substitution). The data were obtained in the presence of 0.01 *M* picric acid.

Table I
Initial Rate Constants for Bromide Ion Production from RMe_2CBr in DMF

Entry	R	Temp, °C	C_0,[a] *M*	Additives[a]	10^6k_1, sec^{-1}
1	Me	25.0	0.0390		2.3_1
2	Me	25.0	0.0412		2.1_7
3	Me	30.0	0.0375		4.2_8
4	Me	30.0	0.0385		4.2_9
5	Et	25.0	0.0332		5.2_3
6	Et	25.0	0.0482		5.1_1
7	Et	25.0	0.0482		5.1_8
8	Et	30.0	0.0342		8.5_7
9	Et	30.0	0.0345		8.4_3
10	Pr	24.8	0.0261		5.6_7
11	Pr	27.4	0.0323		7.1_6
12	Pr	29.9	0.0292		9.5_3
13	Pr	30.0	0.0317		9.6_7
14	Pr	29.9	0.0331		9.6_7
15	Pr	30.0	0.0468		9.6_0
16	Pr	30.0	0.0468		9.8_3
17	Pr	30.0	0.0470		9.6_0
18	Pr	30.1	0.1160		9.6_0
19	Pr	45.0	0.0448		47.9
20	Pr	60.0	0.0202		262
21	Pr	60.0	0.0207		245
22	Pr	30.0	0.0320		9.2_3
23	Pr	30.2	0.0336		9.8_7
24	Pr	30.0	0.0890		11.1_1
25	Pr	30.0	0.0898	0.2 *M* 2,6-lutidine	10.9_9
26	Pr	30.0	0.0309	0.1 *M* $NaNO_3$	11.3_4
27	Pr	30.0	0.0325	0.0195 *M* NaN_3	16.0
28	Pr	30.0	0.0340	0.060 *M* NaN_3	40.1
29	Pr	30.0	0.0409	0.075 *M* NaN_3	46.7
30	Pr	30.0	0.0356	0.093 *M* NaN_3	52.2
31	Pr	30.0	0.0345	0.060 *M* NaN_3 + 0.100 *M* $NaNO_3$	38.6

[a] In the presence of 0.010 *M* picric acid, except for runs 22, 23 (0.004 *M*) and 24, 25 (no picric acid added).

quired, to obtain a residual potential difference of the order of 1 mV between both electrodes. As this disparity was shown to be dependent on C_{Br^-}, the electrodes are placed, at regular intervals, in the same vessel to allow comparison in the course of a kinetic run.

Measurement of potential differences was effected by means of a Radiometer Copenhagen Type PHM 22 p pH meter, as a coarse indicator and as an amplifier of high-input impedance, coupled to a recording electrometer Heath EUW-301, thus allowing recording with a precision of better than 0.03 mV if needed. A Leeds and Northrup No. 7645 potentiometer was employed to measure and to compensate the initial disparity between the electrodes.

Determination of Reaction Rates. The reaction is started by injection of an approximately known amount of substrate into the solvent in the reaction vessel, containing, besides 10^{-3} *M* $AgBr_2^-$, any additions desired. To obviate the effect of a certain sluggishness of the electrodes, addition of excess titrant is always made in advance, and the moment at which equality is reached, noted from the recording.

At the end of the run (usually not more than 3% conversion) 2-ml samples are collected and bromide ion is determined by potentiometric titration with aqueous $AgNO_3$, after alkaline hydrolysis.

First-order rate constants were directly calculated from the slopes of ln $(a - x)$ *vs.* t plots, where a is the initial substrate concentration and x is the bromide concentration in the titration vessel as derived from the known addition of titrant (0.5 *M* NaBr in DMF). No correction was applied for incomplete dissociation of HBr, as it was shown previously that the initial reaction corresponds largely to substitution in which no acid is produced.[1] From experimental tests, where formation of HBr was simulated, it was deduced that even the hypothesis of total elimination would lead to rate constants higher by only 2–3%.

Materials. Purification of the solvent and synthesis of 2-bromo-2-methylpentane have been previously reported.[1]

tert-Butyl bromide and *tert*-amyl bromide were obtained through reaction of the corresponding alcohol with PBr_3 at −20° and purified by fractionation under reduced pressure. All bromides were redistilled under reduced pressure immediately prior to use.[9]

Reliability of the Method. The method was empirically tested by titration in both vessels with the same titrant and comparison of the amounts needed to restore potential equilibrium. In the range of 2×10^{-4}–3×10^{-2} *M* the mean deviation was 0.8%. As every kinetic determination was made on the basis of at least 10 data points, it is felt that the precision obtained is still increased by the statistical distribution. The values of the standard deviations in the case of multiple determinations (*vide infra*) support this treatment.

Calculation of Total Solvolysis. An approximate calculation of total solvolysis was performed on the basis of a system composed of first-order and a second-order autocatalytic reaction

$$A \xrightarrow{k_1} X + Y$$

$$A + X' \xrightarrow{k_2} X + X' + Z$$

where A is the substrate, Y and Z are reaction products which may or may not be identical, and X′ represents the active reagent (*e.g.*, Br^-) in equilibrium with X, which summarizes all species in the same equilibrium (*e.g.*, $HBr + Br^- + \frac{1}{2}HBr_2^-$ etc.).

If a constant ratio $\alpha = C_{X'}/C_X$ is assumed, the system gives rise to the differential equations $dx/dt = dy/dt + dz/dt = k_1(a - x) + k_2(a - x)\alpha x$ or $dx/(a - x)(1 + r\alpha x) = k_1dt$, if $k_2/k_1 = r$ and where $a = C_{A,\text{initial}}$ and x, y, and z represent concentrations of the species X, Y, and Z, and $dy = dx/(1 + r\alpha x)$. On integration these yield

$$[1/(1 + r\alpha a)] \ln [(1 + r\alpha x)a/(a - x)] = k_1t$$

and

$$y = (1/r) \ln (1 + r\alpha x)$$

allowing calculation of x, y, and $z = x - y$. In the calculation of solvolysis (in presence of 0.01 *M* picric acid) the following values of the rate constants were utilized: $k_1 = 1.0 \times 10^{-5}$ sec^{-1} (instead of 0.97×10^{-5} sec^{-1}, to account for the small rise in ionic strength in the course of the reaction) and $k_2 = 4.0 \times 10^{-4}$ l. mol^{-1} sec^{-1}.[1]

It should be noted that in reality α is not a constant ratio and that it is not known with any certainty, due to the as yet incomplete knowledge of the ionization equilibria of HBr in DMF. Another difficulty resides in the probable importance of HBr_2^- as a major ionization product and its importance as a kinetic base, for which the corresponding rate constant k_{2,HBr_2^-} cannot be estimated. Some measurements on the HBr equilibrium and the provisional assumption $k_{2,Br^-} = k_{2,HBr_2^-}$ allow a crude estimate of $\bar{\alpha} = \bar{\alpha}_{Br^-} + \bar{\alpha}_{HBr_2^-} k_{2,HBr_2^-}/k_{2,Br^-}$ to be made. This value was altered by trial and error until the simulated curve remained between the limits set by the titration results (see Figure 1). The chosen value was 0.55, well within the range of the values estimated on the

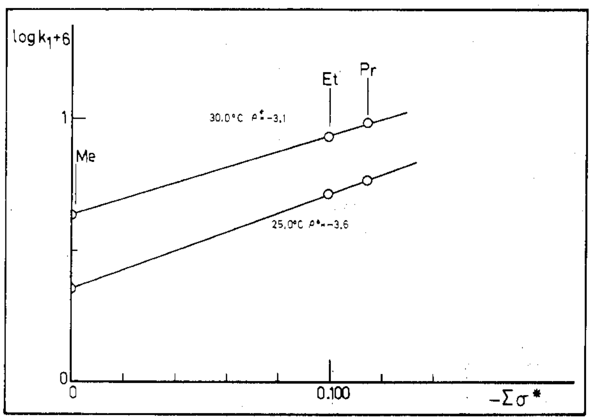


Figure 2. Taft–Hammett correlation for initial solvolysis rates of RMe_2CBr in DMF (0.01 *M* picric acid added) for R = Me, Et, Pr.

above assumptions (time average over the reaction course determined by direct estimation was found to be 0.47).

In spite of the seeming arbitrariness we feel confident that the procedure followed will not lead to large deviations from reality, as in the interval considered the total solvolysis is determined to the extent of 80–100% by the more accurately known first-order reaction. Also, bromide ion is initially the most important base formed and is suspected to remain so for appreciable time. Thus, the slope of the calculated curve fits the experimental course of the reaction very well, once the elimination becomes the sole net reaction.

Results

Reaction Rates. With the exception of two runs, all experiments have been executed in the presence of added picric acid. Apart from its promotion of electrode response, it was felt that the values obtained in this way are more likely to reflect the true rate constant in the course of the reaction, when acidity and ionic strength will have attained comparable levels. They also are directly related to the experiments in the preceding paper,[1] where addition of 10^{-2} *M* picric acid has been used.

Choice of substrate, reaction conditions, and the ensuing rate constants are summarized in Table I. Only data pertaining to the first 2–3% of the conversion have been considered for calculation. A second-order contribution to the total rate can be estimated to be at most 1% and therefore has not been corrected for.

The only value that allows comparison with literature data is for *t*-BuBr at 25.0°. It compares favorably with that reported by Kornblum and Blackwood[10] ($2.3_8 \times 10^{-6}$ sec^{-1}) and by Ross and Labes[11] (2.6×10^{-6} sec^{-1}). It was expected that our value ($2.2_4 \times 10^{-6}$ sec^{-1}) would be lowest as our measurements are confined to the first 3% of the reaction, thus excluding any important second-order contribution. Cook and Parker[12] obtained a high value ($3.3_7 \times 10^{-6}$ sec^{-1}) which can hardly be ascribed to the presence of 0.12 *M* NEt_4ClO_4, as we found only a 17% increase on addition of 0.100 *M* $NaNO_3$ in the solvolysis of **1**.

Influence of Substrate Concentration. Variation of substrate concentration by a factor 4 had no statistically significant effect on rate constants. The mean value of k_1 for runs 12–18[13] (R = Pr; temperature 30°) was found to be $(9.66 \pm 0.12) \times 10^{-6}$ sec^{-1} with substrate concentration ranging from 0.0292 to 0.1160 *M*.

Activation Energy. The activation energy E_a for the solvolysis of **1** was calculated to be 90.4 ± 0.8 kJ mol^{-1}, assuming a linear log k_1 *vs.* $1/T$ relation. The following activation parameters were found: $\Delta H^* = 87.9 \pm 0.8$ kJ mol^{-1} and $\Delta S^* = -52 \pm 4$ J K^{-1} mol^{-1}. The data of Ross and Labes[11] allow calculation of the same parameters for *t*-BuBr to give 87.4 kJ mol^{-1} and −59 J K^{-1} mol^{-1} and the rate difference is thus shown to be ascribable to an entropy effect only. The activation enthalpy in DMF is lower by a few kilojoules per mole than the corresponding parameter in pure protic solvents,[14] but comparable to it in mixed protic–aprotic solvents,[14] *e.g.*, dioxane–water and acetone–water. It may be noted in this connection that the aprotic solvents cited are known to possess nucleophilicity and could possibly participate in the transition state. We note in this context the difference in the corresponding values for acetonitrile[15] and for nitromethane;[16] 93.3 and 83.7 kJ mol^{-1}, respectively; the former is known to be a much weaker nucleophile.

Influence of Substrate Structure. Although three substrates evidently represent too small a choice to prove the existence of a linear relationship, it was thought worthwhile to represent our results in the form of a Taft correlation (Figure 2). Derived ρ^* values are −3.6 and −3.1 at 25 and 30°, respectively. They compare very well with the value −3.29 obtained by Streitwieser[17] from a huge amount of data with respect to the solvolysis of tertiary alkyl halides in 80% ethanol. It is customary to take similar values as an indication of appreciable development of positive charge on C_α in the transition state.[17,18]

Influence of Added Acid and of Ionic Strength. Reduction of the picric acid concentration from 0.010 to 0.004 *M* resulted in a decrease in reaction rate of at most 3%. This clearly demonstrates that acid catalysis can safely be excluded. That the eventual decrease is to be seen as an ionic strength effect is corroborated by the 17% increase noted, after addition of 0.1 *M* $NaNO_3$.

A similar salt effect is in accord with the theoretical expression derived by Bateman[19] for the reaction of a neutral molecule and characterized by a dipolar transition state

$$\ln (k_1/k_{1,\,0}) = (8\pi Ne^2/1000DkT)^{1/2}Z^2d\alpha I$$

where *e* is the charge of the electron, *D* the dielectric constant, *k* the Boltzmann constant, *Z* the fractional charge on each pole, *d* the distance between them, and $\alpha = 0.509 \ln 10$. Insertion of the data yields $Z^2d \doteq 0.97$ Å, a reasonable value, comparable to 0.78–0.82 Å found by Bateman for *t*-BuBr in 90% acetone.[19]

Solvolysis in Absence of Added Picric Acid. Extrapolating from results at different ionic strength, a value of 9.5×10^{-6} sec^{-1} should have been expected for the *initial* solvolysis rate constant of **1** at 30° in the pure solvent. The rates observed (with and without lutidine added) are 17% higher instead! Because of the simultaneous peculiarity of the product distribution, described in the preceding paper, we are inclined to interpret this difference as due to a separate reaction which seems to be inhibited at higher ionic strength.

Effect of Added NaN_3. Addition of sodium azide to solvolyzing mixtures has been used in the past to exclude the possibility of nucleophilic solvent assistance.[20] It has generally been assumed that when the strongly nucleophilic azide ion failed to enhance the reaction rate, participation of the solvent as a reagent had to be excluded also.

Runs 27–31 show in a convincing way that this is not the case in DMF even for a tertiary alkyl halide. Figure 3 shows a plot of $k_{1,N_3^-}/k_{1,0}$ *vs.* $(C_{NaN_3} - C_{\text{picric acid}})$,[21] where k_{1,N_3^-} is the pseudo-first-order rate constant in the presence of azide ion.

The curve obtained is reminiscent of those presented by Sneen and coworkers[22] to provide proof for the ion-pair theory of S_N2 reactions. A comparable analysis will not be attempted here, as we have no precise knowledge of the ion association equilibria and some conductivity measurements on azide solutions incite us to caution. Anyway, it seems probable that azide ion participates in a second-order reac-

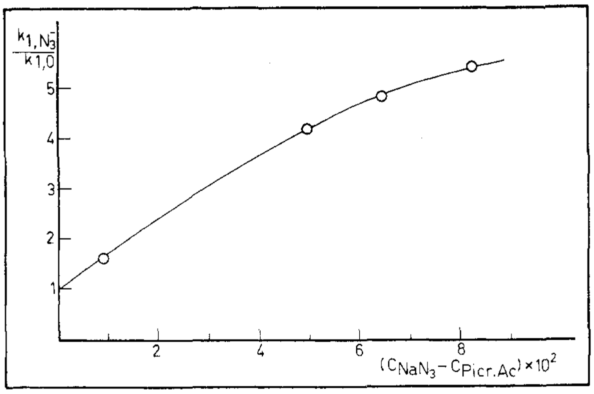


Figure 3. Influence of added sodium azide on bromide ion production from $PrMe_2CBr$ ($C_0 \approx 0.03$ *M*; 0.01 M picric acid added) in DMF at 30.0°.

tion with the tertiary substrate 1 and of which about 30–50% may be considered SN2! This cannot, of course, be used to prove solvent participation, but it emphasizes its possibility.

General Remarks. The initial solvolysis of simple tertiary alkyl bromides in DMF strongly resembles the analogous reactions in protic solvents in many of its features, *e.g.*, the dependence on substrate structure and on ionic strength. On the other hand, though no conclusive evidence was given, nucleophilic interaction between solvent and substrate would well fit the picture.

Solvolysis of 2-Bromo-2-methylpentane. Comparison of Calculated Solvolysis with Other Experimental Data. The potentiometric compensation method, described in this paper, readily follows the evolution of bromide ion concentration. As a consequence of the production of acid attending elimination and of incomplete ionization of HBr, it is only at the start of the solvolysis that the Br^- concentration can be taken to be equivalent to the total reaction rate. A direct comparison of the experimental data is therefore excluded except for the first minutes of the reaction. Even so, an interesting conclusion can be drawn with regard to the presence of appreciable amounts of "ion pairs" at the onset of the solvolysis. Further comparison is better attempted by use of the calculated course of reaction based on the determined or estimated rate constants. Figure 1 summarizes some results with respect to the solvolysis of approximately 0.1 *M* 1 in DMF at 30° and with 0.01 *M* picric acid added, as described in the previous paper.[1]

Curves a and b are based on titration data obtained after a distributive extraction with CCl_4–water, curve a prior to and curve b after a 5-min residence time in CCl_4. Curve b was thought to represent total elimination while curve a stood, in addition, for any extractable solvolysis product, ionic intermediate, *and* extractable ion pairs included. To this picture is added the calculated curve c, denoting elimination plus formation of an ionic substitution product $RDMF^+$ (7).[23]

This juxtaposition allows further insight into the details of the solvolysis, as now the evolution of the concentration of 7 can be viewed separately from that of possible ion pairs. This is shown more clearly in Figure 4 which reproduces (a) the evolution of C_7, (b) $C_{\text{"extractable ion pairs"}}$, (c) the first-order contribution to solvolysis, and (d) the part of the former curve corresponding to elimination.

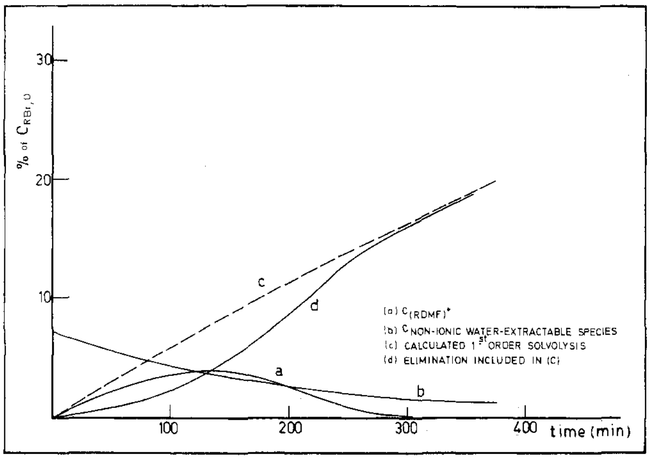
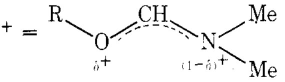


Figure 4. Analysis of the first-order component in the solvolysis of 1 in DMF at 30.0°. All curves are calculated from the data referred to in Figure 1.

In the previous paper[1] the existence of the cationic intermediate 7 has been anticipated. Figure 4 discloses that it is the principal, if not the only, initial solvolysis product. It accumulates till a maximum value of 4% of the substrate concentration. The rate of its decomposition to olefins increases steadily until most of the intermediate has disappeared.

Another notable feature is the continuous decrease of the amount of extractable "ion pairs," which is highest at very short reaction times. It cannot be estimated with confidence how much of it remains after the disappearance of **7**, but it seems to be established that the rate of decrease is slowed down considerably from about that moment. Both features will be commented upon separately in the following paragraphs.

The Substitution Product RDMF$^+$ (7) and Its Decomposition. Instead of the proposed structure, 7 might be

RDMF$^+$ =


viewed as a solvated carbenium ion. Later in this paper, however, more evidence will be presented to show the relative unimportance of dissociated carbenium ions in the overall scheme. The existence of similar substitution products has already been assumed by Kornblum and Blackwood[10] after observing halide ion production in DMF solutions of methyl iodide or benzyl bromide.[24] The formation of stable salts between solvent and alkyl halides has also been described for DMSO.[25] Moreover, nucleophilic participation of DMF is really not surprising, considering the role attributed to less nucleophilic molecules such as *p*- dioxane and acetone in the solvolyses of 2-octyl brosylate in 75% dioxane–water[26] and 80% acetone–methanol,[27] respectively.

Comparison of the slope of curve d and the corresponding values of C_7 (a) in Figure 4 clearly counterindicates a first-order decay of 7. Indeed, the latter curve reaches a maximum at approximately 125 min whereas curve d is steepest somewhere around the 200-min point. Therefore, kinetic involvement of a reaction product, *e.g.*, of the bromide ion, is highly probable. If we take $[Br^-]$ to be proportional to the total solvolysis, the product $[C_7][Br^-]$ has a maximum at 180 min and $[C_7][Br^-]^2$ even at 195 min, both much better in accord with the behavior of curve d.

One can think of several reasonable mechanisms, in accord with the facts known so far.

1. **E2 Decomposition of 7 with Br$^-$.** This mechanism would be reminiscent of E2 eliminations of "onium" compounds. These mechanisms are known to be subject to inductive control, attended by a typical Hofmann orientation.[28] Delocalization of positive charge, as in **7**, would be

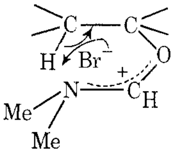
$$7 + Br^- \longrightarrow \text{olefins} + \text{DMF} + \text{HBr}$$

expected to deemphasize this trend, so that there is no obvious disagreement with an observed product distribution of 41–46% terminal olefin.

2. First-order Elimination of the Corresponding Ion Pair 6. The situation depicted here will be kinetically equivalent to the former in a number of cases.

$$7 + \mathrm{Br}^- \underset{k_-}{\overset{k_+}{\rightleftarrows}} \underset{6}{7||\mathrm{Br}^-} \xrightarrow{k'} \text{olefins} + \mathrm{HBr} + \mathrm{DMF}$$

If $k_- \gg k'$ the concentration of the ion pair and consequently the elimination rate are determined by the product [**6**][Br$^-$]. This version finds support in the surmise that at least a substantial fraction of the ion pairs disappeared simultaneously with **6**. If on the other hand the decomposition of the ion pair is much faster than its formation, it will not be found in measurable quantities, but the kinetic order of the elimination will remain the same with respect to **7** and Br$^-$. First-order elimination of **6** could very well take place *via* an "internal" mechanism akin to Ei.



Of course, a second-order dehydrobromination of **6** or some other third-order process cannot be excluded.

Olefin distribution studies do not allow us to choose between the cited alternatives, as none is expected to possess an outspoken Saytzeff regiospecificity.[28]

Nature of the Ion Pairs. A most remarkable finding was the impressive amount of nonionic water-extractable species,[1] present in the solvolyzing DMF solution. Apparently, these particles hold strongly to the solvent molecules, as even addition to excess CCl_4 only results in a relatively slow recombination. In the course of the distributive extraction they are carried into the aqueous phase, where they are hydrolyzed subsequently.

It would appear to us that solvent-separated ion pairs are the most likely candidates to show this behavior. Part of these may be RDMF$^+$||Br$^-$ (**6**), as suggested above, possibly along with R$^+$||Br$^-$ (**3**). Neither of these, however, can be responsible for the large amount present at the very start of the reaction! In a solution of 0.1 *M* **1**, this totals 6–7% in presence of 0.01 *M* picric acid, against 22% in absence of any additive. As the solvolysis rate is not substantially different, it seems excluded that it is due to any ion pair which is to be considered as lying on the reaction path(s) leading to solvolysis. If that were the case, solvolysis kinetics would evidently be expected to be greatly influenced by the extent of its initial accumulation and by its subsequent diminution. Although satisfactory evidence is still wanting, we would like to retain, as a possible structure, the dipolar complex of the alkyl halide (or corresponding intimate ion pair) with a solvent molecule (**5**). The responsible dipole–dipole interactions may be expected to be appreciably weakened by increasing ionic strength, thus providing an explanation for the influence of added picric acid on the ion-pair concentration and for its relatively fast decrease in the course of the reaction.

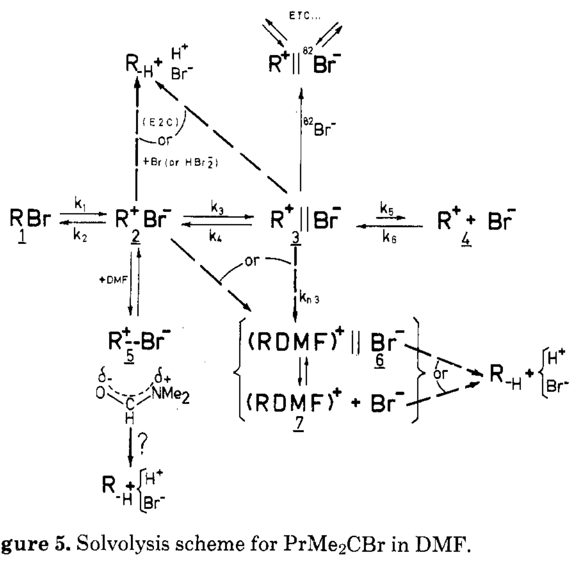
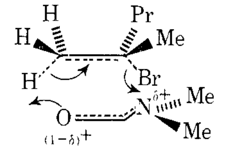


Figure 5. Solvolysis scheme for $PrMe_2CBr$ in DMF.

Another indication for the existence of a side branch of the main pathway is to be found in *in the rapid transfer of initially incorporated* ^{82}*Br to a water-extractable form.*[1] A rate constant for this process is estimated to be at least 60 times greater than that of the solvolysis itself. This suggests that it relates to a transfer to an undissociated form and adds further credibility to the existence of the already proposed species **5**. In fact it is quite plausible that in both cases the formation of the same water-extractable species is concerned, for which the structure of a dipolar complex was proposed. One more comment can be made, *viz.*, upon the extra amount of initial solvolysis and the higher proportion of terminal olefin observed in total absence of ionic additives.[1] Both phenomena could possibly be ascribed to a direct elimination of **5**, appreciable only at the start of the reaction. For the proposed structure a way of elimination is readily conceived with the associated solvent molecule acting as a base. The transition state might resemble the structure



The ensuing syn elimination would account for a probable Hofmann orientation (possibly 70–100% 1-ene).[28]

A Hypothetical Solvolysis Scheme for $PrMe_2CBr$ in DMF. Based on all presented evidence, we will attempt to sketch a solvolysis scheme (Figure 5) as a means of showing more clearly the emerging facts and to pinpoint some of the remaining question marks. Where alternative paths are available and no definite choice could be made, all were drawn in dashed lines. Some SN2 reactions thought to possess a common intermediate were also indicated. The *presence* of the species **5** and **6** is thought to be essential for the explanation offered, although the structures presented for them have no very firm foundation yet. The description which follows refers to the solvolysis of **1** in DMF under the conditions of our experiments, but up to a certain point probably to tertiary alkyl halides in general.

Following dissolution of the substrate, a very fast dynamic equilibrium is set up between the different species of the Winstein scheme (**1**–**4**).[29] The "equilibrium" concentration of dissociated carbenium ions R$^+$ (**4**) is thought to be much lower than in protic media and the amount of solvolysis occurring through this intermediate negligible. Solvolysis is probably attended by the ion pairs **2** and **3** reaching higher concentrations.

Especially at low ionic strength, an important accumulation of a nonionic product (**5**) is noted, to which the tentative structure of a dipolar complex has already been assigned. A relatively slow elimination of **5**, with a high yield of terminal olefin may be possible. The concentration of **5**

Table II
Solvolysis Rates of *t*-BuX (X = Cl, Br) in Different Solvents at 25.0°

Run	Solvent	$-\log k_1$ X = Cl[a]	$-\log k_1$ X = Br[b]	$-\Delta \log k_1$
1	H_2O	1.54	0.11	1.43
2	$EtOH-H_2O$ (80 : 20)	5.03	3.45	1.58
3	MeOH	6.12	4.48	1.64
4	AcOH	6.71	5.52	1.19
5	EtOH	7.07	5.36	1.71
6	$MeNO_2$	8.12[c]	5.44[d]	2.68
7	DMF	8.48[e]	5.64[f]	2.84
8	MeCN	8.73[g]	5.90[h]	2.83
9	Me_2CO	9.9[i]	7.13[j]	2.8

[a] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956), except when indicated otherwise. [b] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957), except when indicated otherwise. [c] Y. Pocker, *J. Chem. Soc.*, 1972 (1960). [d] P. B. D. de la Mare, *et al.*, *ibid.*, 2930 (1954). [e] S. D. Ross and M. Labes, *J. Amer. Chem. Soc.*, **79**, 4155 (1957). [f] This work. [g] M. H. Abraham, *J. Chem. Soc.*, 1343 (1972). [h] H. M. R. Hofmann, *ibid.*, 6753 (1965). [i] Cited in ref *g*. [j] S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Lett.*, **No. 16**, 24 (1959).

decreases rapidly as the reaction proceeds, probably by reversal of its formation, in answer to the changed environment.

At the same time a more important production of inorganic bromide accompanies the formation of the cationic product **7**, in what may be considered to be the rate-determining step. Product **7** arises probably through collapse of the solvent-separated ion pair **3**, almost certainly *via* the (likewise solvent-separated) ion pair **6**, which may be in a rapid equilibrium with **7**. Product **7** accumulates at first but undergoes in its turn an elimination reaction in a way kinetically dependent on Br^- (or possibly HBr). The increasing concentrations of Br^- and HBr_2^- cause a reaction of steadily growing importance. Being kinetically strong bases in DAS, they give rise to autocatalytic E2 with a notable Saytzeff orientation (16% 1-ene). Especially at high substrate concentration, these reactions will ultimately dominate the entire solvolysis picture.

The Insignificance of Carbenium Ions as Intermediates. To explain radiobromide incorporation data, it was postulated[1] that the concentration of free carbenium ions decreases rapidly within the first minutes of solvolysis, as a consequence of enhanced ion return caused by the growing bromide ion concentration. As an important corollary, it follows that the rate of solvolysis, if it occurred by the classical carbenium ion pathway, would simultaneously show a dramatic downfall, which is not the case at all.

The Rate-Determining Step of Solvolysis. From the incorporation experiments it was concluded that the Winstein equilibria are presumably composed of reactions which are appreciably faster than total solvolysis.[1] Therefore, they are not believed to comprise the rate-determining step. As the intermediacy of dissociated carbenium ions is excluded, the step at issue may well be the collapse of an ion pair, most probably a solvent-separated one. As a matter of fact, the latter is expected to show sufficient reactivity toward the *solvent*, almost as much as a free carbenium ion. It is likely that in this case the formation of a likewise solvent-separated ion pair **7** $\|Br^-$ (**6**) will precede the appearance of **7**. Sneen's description of an intimate ion pair, as being merely a compound possessing an extended bond with considerable ionic character,[22] does not meet universal consensus. Yet, the presence of an appreciable amount of covalent bonding is generally accepted. Consequently, the geometry at C_α may be not too remote from the original sp^3 hybridization, and in a tertiary substrate such as **1**, considerable steric hindrance to the necessarily back-side substitution is to be anticipated. These are however arguments which stem from generally accepted ideas, not from experimental data.

For solvolysis in protic media, the exact location of the rate-determining step is not generally known, although it is usually assumed to be included in the Winstein scheme. From the analysis of accurate data on the hydrolysis of *t*-BuCl, Scott and Robertson[30] suspected it to be the formation of the solvent-separated ion pair. This suggests that, even in our case, where it is not the slowest step, it may still be of great importance in determining the steady-state concentration of **3** and thereby influencing the observed rate. In this connection we wish to point out the remarkable differences in selectivity toward the leaving group, displayed in solvolysis rates, when one turns from protic to DAS media. From Table II it can be derived that in general the rate ratio $k_{t\text{-BuBr}}/k_{t\text{-BuCl}}$ is 15 times greater in the latter. The systematic way in which this difference occurs indicates a fundamental change. The fact that nucleophilic power of the solvent does not seem to be of much influence is not in contradiction with our views, as the collapse of a solvent-separated ion pair is not expected to show much selectivity with regard to the solvent. The large effect of a change in leaving group (Cl^- *vs.* Br^-) can be attributed to the position of the equilibrium **2** $\rightleftarrows$ **3**, which in DMF lies undoubtedly more to the left for the chloride ion, due to its smaller aptitude for solvation.[31]

Affinity with Sneen's Unified Ion-Pair Theory. In DMF appreciable and directly measurable quantities of different kinds of ion pairs were shown to be present during solvolysis of tertiary alkyl bromides. This alone would suffice to draw our attention to their potential role in the mechanisms involved and in related ones where these substrates are used in the same solvent. It appears to us that DAS might prove to become the media of choice for the study of ion-pair mechanisms.

In 1969 Sneen and Larsen published a unified theory of nucleophilic substitutions[32] and eliminations[33] in which they posited ion pairs to be common intermediates in all reactions cited, second order and first order alike. Since then, though, the generality of concept has been challenged;[34] several independent authors have brought forward supporting evidence in definite cases.[35]

Our analysis of the solvolysis of **1** in DMF resembles in many points the general scheme for solvolysis as presented by Sneen in a recent publication.[22] As all evidence pro and con has hitherto been obtained by use of protic (or mixed) solvents, our results clearly cannot decide in any issue in debate. The fact, however, that in a favorable solvent such as DMF solvolytic phenomena can be efficiently described in terms of mechanisms which overlap to a large extent with the scheme developed by Sneen does support its claim to a fundamental generality.

In the same recent review[22] Sneen described the probable conditions for the occurrence of a nucleophilic attack at the various points of the Winstein scheme. He thereby predicted reaction at the level of the solvent-separated ion pair to take place when the incipient carbenium ion center is rather stable and possesses a hindered back side. These are precisely the characteristics to be expected with **1** as a substrate and we are inclined to say that the prediction is borne out, at least with DMF as a solvent. Sneen and coworkers[22] made repeated use of methods in which some nucleophilic reagent (especially N_3^-) was added, and the reaction rate and selectivity were studied as a function of its concentration. Its adaptation for use in DAS is rendered difficult by the insufficiently known association equilibria of the mostly ionic reagents, by their enhanced basicity, and by the possible reactivity of their ion pairs.

Ion Pairs as Possible Direct Substrates in E2C Reactions. Once it is accepted that ion pairs are more likely to undergo nucleophilic attack than the undissociated substrate, it may be expected that, at least in some cases, they are preferred to the latter in elimination reactions also. One might wonder if the prevalence of DAS as media for E2C reactions should not be ascribed to their proficiency at generating ion pairs. Some of the most notable characteristics of E2C,[36] such as the absolute trans elimination and a "loose" transition state, become self-explanatory, when ion pairs are considered as the direct substrates.[37,38] Research in progress in our laboratory indicates that the E2 reaction of tertiary alkyl bromides with bromide ion is competitively inhibited by added azide ion.

Registry No.—1, 4283-80-1.

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(23) Numbers were assigned to the different species and intermediates, in accordance with their place in the scheme (see Figure 5) presented in this paper, not with the chronology of appearance in the text. Product **7** is identical with structure **2** in the previous paper.[1]
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Kinetics of the Oxidative Cleavage of α-Phenylbenzoins by Alkaline Hypobromite in Aqueous Dioxane[1]

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Oxidative cleavage of α-phenylbenzoins $[Ar^1Ar^2C(OH)COAr^3]$ by hypobromous acid to give benzophenones and benzoic acids has been studied kinetically in alkaline 50 vol. % aqueous dioxane. The effect of ring substituents on the rate at 25° gives ρ values of +2.8 for the σ values on Ar^3 and +2.3 for the sum of σ values on Ar^1 and Ar^2. A mechanism is postulated, which involves the formation of hypobromite ester of substrate followed by a rate-determining attack of hydroxide ion on the carbonyl carbon to give the products.

Several papers were published on the oxidation of alcohols by halogen to carbonyl compounds.[2–4] The workers in the mechanistic studies of these reactions were interested mainly in speculation of the transition state, attacking agents, and their relative reactivities. There are a number of evidences[2] that the halogen oxidation of alcohol in acidic solutions occurs *via* a rate-determining abstraction of α-hydride ion by molecular halogen. On the other hand, for the oxidation by alkaline hypohalite, the intermediacy of hypohalite ester of substrate was postulated in some oxidations of alcohols, *i.e.*, the oxidation of alcohols[3] and the oxidative decarboxylation of α-hydroxycarboxylic acids.[4]

The oxidative decarboxylation of α-hydroxycarboxylic acids by alkaline hypohalite in an aqueous solution was re-